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SYNTHESIS OF SEMICONDUCTING COORDINATION COMPOUNDS. (U)
JAN 77 G N SCHRAUZER

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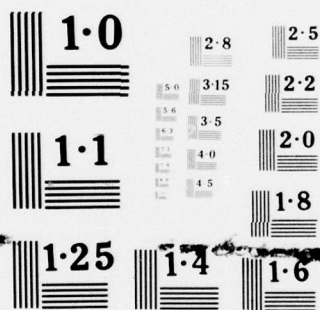
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FINAL TECHNICAL REPORT

Project Title: Synthesis of Semiconducting Coordination Compounds

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SUMMARY PROGRESS REPORT

The work during the tenure of the grant has been completed and is summarized as follows:

(1) Synthesis of superconducting compounds by thermolysis of volatile hydrides and of organometallic compounds on glowing wires.

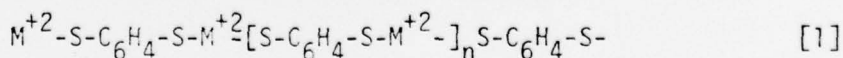
New methods for the synthesis of superconducting phases are always needed. We therefore became interested in preparing superconducting binary compounds directly on wires through the thermal decomposition of volatile hydrides and organometallic compounds. This method was chosen as it would yield the superconducting phase deposited on wires which could be employed directly. This work was successful and led to the synthesis of high-temperature superconducting phases in the Nb-Ge, Nb-Sn, V-Si, V-Ge, V-Sn and Mo-C system. For face-centered cubic NbC a higher transition temperature than previously reported was obtained. Samples of Nb₃Ge with a T_c onset of 15.8°K were also synthesized in this manner. Having demonstrated the general usefulness of this method the results were published [G.N.Schrauzer and H.Prakash, Solid State Commun. 14, 1259 (1974)].

(2) Discovery of a superconducting phase in the Li-Ti-O System.

H.E.BARZ et al [Science 175, 884 (1972)] recently reported on a ternary systems in the Li-Ti-S systems having rather high superconducting transition temperatures. We became interested in this system as it was related to some of the projects to be studied under the present grant. When attempts were made to prepare phases in the Li-Ti-S system we discovered a new superconducting phase which, surprisingly, was not due to a sulfur containing compound. It was instead identified to belong to a contaminant belonging to a spinel phase in the Li-Ti-O phase. The compound has the composition Li_{1+x}Ti_{2-x}O₄ and has a face-centered cubic structure. The superconducting temperatures of this phase range from 7 to 13.7°K. [Mat.Res.Bull., 8, 777 (1973); D.C.Johnson et al.]

(3) Synthesis and Electrical Properties of Transition Metal Mercaptides of 1,4-Dimercaptobenzene.

The synthesis of new semiconducting polymeric compounds or complexes was one of the major goals to be reached under the present contract. Following previous work on the synthesis and electrical properties of complexes with unsaturated 1,2-dithiol ligands we extended our efforts to the synthesis of complexes or mercaptides of 1,4-dimercaptobenzene. We expected that this ligand would produce polymeric compounds having the generalized structure [1]



Several of these mercaptides of different metals behave like semiconducting polymers within the temperature range investigated. An interesting result is the relatively low electrical resistivity (40 ohms cm at 25⁰) of the Cu(I)-complex of composition $[\text{CuSC}_6\text{H}_4\text{SCu}]_n$. Copper thiophenolate, $[\text{C}_6\text{H}_5\text{SCu}]_n$ is found to behave like a semiconductor as well, with an electrical resistivity of 5.1×10^4 ohm cm at 25⁰. We also studied the reaction of the copper complexes with 7,7,8,8-tetracyano-p-quinodimethane (TCNQ) in an effort to obtain metal-like charge transfer complexes related to the tetrathiafulvalene-TCNQ complexes. However, our compounds reacted with TCNQ with cleavage of the Cu-S bonds and the formation of the Cu(I)-salt of the TCNQ radical anion, $\text{Cu(I)}-\text{TCNQ}^-$. In addition to copper complexes, we prepared polymers containing Pb, Ag, Hg and Ni as the metallic component. The electrical resistivities of these polymers decreased in the order $[\text{Cu}]$, Ag, Ni, Hg, Pb. G.N. Schrauzer and H. Prakash, Inorganic Chemistry 14, 1200 (1975).

(4) Complexes of 1,2,4,5-Benzenetetrathiol and 1,2,4,5-Benzenetrithiol.

Extending the research outlined in part (3) of this report, coordination compounds of 1,2,4,5-benzenetetrathiol and of 1,2,4-benzenetrithiol were synthesized analogously. The electrical properties of the complexes are compared in TABLE I.

TABLE I
Room Temperature Resistivities of the Coordination Complexes of Polythiols

Metal Ion	1,4- $\text{C}_6\text{H}_4(\text{SH})_2$	1,2,4- $\text{C}_6\text{H}_3(\text{SH})_3$	1,2,4,5- $\text{C}_6\text{H}_2(\text{SH})_4$
Cu(I)	184 ohm cm	3.9×10^5 ohm cm	22 ohm cm
Cu(II)	3.5×10^8 ohm cm	1.2×10^6 ohm cm	1.4×10^3 ohm cm
Ni(II)	ca. 10^9 ohm cm	3.7×10^4 ohm cm	5.0 ohm cm

The nickel complex of 1,2,4,5- $\text{C}_6\text{H}_2(\text{SH})_4$ with the specific resistivity of 5 ohm cm is one of the most highly conducting coordination polymers known. This work is as yet unpublished but described in greater detail in Technical Report No. 8 (July 2, 1974).

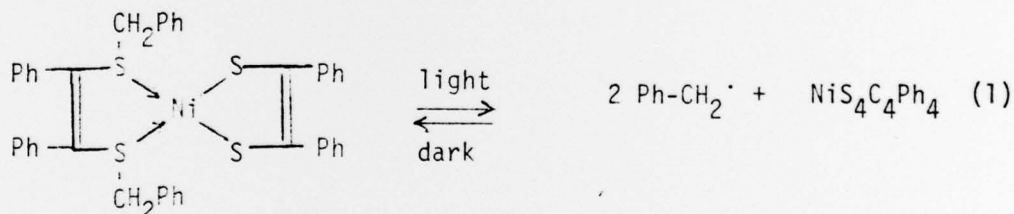
(5) Electrical and Photoluminescent Properties of Substituted Copper(I) Thiophenolates.

Copper thiophenolates possess a polymeric structure and may be regarded to be intermediates between genuine inorganic semiconductors and metallo-organic complexes. Investigating the electrical properties of copper(I)-thiophenolate we noted that the compounds become highly fluorescent when

exposed to ultraviolet light. We prepared a number of substituted copper thiophenolates and studied their optical and electric properties. The following results were obtained: (a) Halogen substituents decrease the conductivity by roughly four orders of magnitude or more. Fluoro-substituted complexes are better conductors than either the chloro- or bromo-complexes. The chloro-substituted compounds are essentially insulators. (b) Further substitution of the bromo-substituted complex in the meta-position by a methyl group results in a slight decrease of the conductivity of the parent complex. This increase is again a reflection of the tendency of the methyl group at the meta position to promote electron transport. (c) Not only inductive or mesomeric effects but also the size of substituents have a profound influence on electrical conductivities of the complexes. (d) All complexes exhibit photoluminescence in the visible region when excited by 3650 Å UV light. Alkyl substituents shift the emission to longer wavelengths, halogen to shorter wavelengths. No photoelectric effects were observed. This work is as yet unpublished & described in greater detail in Technical Report No. 10 (January 8, 1975).

(6) Initial Studies on Reversible Photosensitive Metal Complexes.

The complex $\text{Ni}[\text{S}_4\text{C}_6\text{H}_4]$ can be reduced to a dianion, $[\text{Ni}(\text{S}_4\text{C}_6\text{H}_4)]^{2-}$ which on reaction with benzyl halides is converted into a bis-S-benzyl-derivative. This complex is light-sensitive and when dissolved in transparent plastic becomes a potentially reversible light-sensitive system:



We have investigated the degree of reversibility of reaction (1) and found that it is gradually lost after 50 or more light/dark cycles. The study of another complex containing a norbornene residue attached to the $\text{NiS}_4\text{C}_6\text{H}_4$ moiety did not produce a reversible light sensitive system. Since the response to light was not fast enough for practical utilization, work on these systems was discontinued.

(7) SUMMARY

The discovery of a new superconducting phase, the first in the Li-Ti-O system, was one of the main developments initiated during the tenure of the present grant. The study of the synthesis of superconducting materials through deposition of volatile hydrides or organometallic compound on glowing wires was shown to be practically feasible. Some relatively highly conducting polymeric metal complexes with sulfur containing ligands have been successfully prepared. However, their properties were insufficiently striking to warrant further work in this area.

PUBLICATIONS

- [1] G.N.Schrauzer and H.Prakash: Synthesis of superconducting compounds by thermolysis of volatile hydrides and organometallic compounds on glowing wires. Solid State Commun. 14, 1259 (1974).
- [2] D.C.Johnston, H.Prakash, W.H.Zachariasen and R. Viswanathan: High Temperature Superconductivity in the Li-Ti-O Ternary System. Mat. Res. Bull. 8, 777 (1973). [Supported jointly by contracts # AFOSR/F-44620-72-0017, ONR 053-529 and AEC-AT(04-3)34.
- [3] G.N.Schrauzer and H.Prakash: Synthesis and electrical properties of transition metal mercaptides of 1,4-dimercaptobenzene. Inorganic Chemistry 14, 1200 (1975).